Renewable and Sustainable Energy Reviews 15 (2011) 4171–4186

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

A review of recent laboratory research and commercial developments in fast pyrolysis and upgrading

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ARTICLE INFO

Article history:
Received 6 January 2011
Accepted 5 July 2011
Available online 16 September 2011

Keywords:
Pyrolysis
Biomass
Biofuel
Upgrading
Bio-oil
Thermal conversion

ABSTRACT

Robust alternative technology choices are required in the paradigm shift from the current crude oil-reliant transport fuel platform to a sustainable, more flexible transport infrastructure. In this vein, fast pyrolysis of biomass and upgrading of the product is deemed to have potential as a technology solution. The objective of this review is to provide an update on recent laboratory research and commercial developments in fast pyrolysis and upgrading techniques. Fast pyrolysis is a relatively mature technology and is on the verge of commercialisation. While upgrading of bio-oils is currently confined to laboratory and pilot scale, an increased understanding of upgrading processes has been achieved in recent times.

Contents

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1364-0321/$ – see front matter
doi:10.1016/j.rser.2011.07.035

1. Introduction

Concerns over global warming and finite fossil fuel reserves have led to the realisation that a more environmentally friendly, flexible transport infrastructure is required, that draws on multiple technologies. While solutions with efficiencies that surpass the current combustion engine are likely to be developed, this will take time, and furthermore current consumer preferences favour liquid alkane fuels [1]. It is also likely that liquid fuels will continue to dominate the market for heavy vehicles (ships, aeroplanes, trucks) into the future [2]. Biofuels are seen as a possible solution. Global production of biofuels has increased rapidly to 83 billion litres in 2008, but still retains a small share of the transport fuel market [3]. Some first generation biofuels have encountered significant criticisms over their ability to achieve meaningful substitution, climate change mitigation and economic growth. While more advanced second generation technologies do not completely overcome these problems, they are none-the-less expected to become at least a part of the solution in the shift from fossil resources in the short to medium term [4,5]. It is expected that second generation biofuels will be produced under commercially viable conditions between 2015 and 2020 [5]. Such technologies can be classified as biochemical or thermochemical. While there are no significant advantages of one group of technologies over the other, an added benefit of thermochemical approaches is the ability to yield longer chain hydrocarbons suitable for aviation, marine, or heavy road freight applications [2]. It is has been suggested that biochemical and thermochemical technologies could be employed synergistically in integrated biorefineries with the added benefit of increased flexibility and efficiency [6]. Biomass fast pyrolysis is a component of thermochemical conversion technologies and has a more recent history of development (1980s) than gasification [7]. Thermal decomposition of biomass feedstocks at high heating rates in inert atmospheres yields char, liquid, and gas. While the yield structure is highly dependent on the feedstock and the process conditions employed, liquid (termed 'bio-oil') yields of up to 70–75 wt% from wood can be achieved [8]. One of the main advantages of fast pyrolysis lies in the fact that it is an effective method for densification of voluminous biomass for decentralised densification/centralised conversion platform models [5]. As a biorefinery feedstock bio-oil is very versatile and can be put to other uses apart from the production of biofuels. While bio-oil possesses undesirable fuel properties, it can, be directly applied as a fuel for modified stationary engines. It is widely accepted that the quality of bio-oil from thermal fast pyrolysis cannot be considered a realistic candidate for large scale liquid transport fuel substitution unless it is upgraded. Furthermore, if traditional petroleum fuels like diesel and petrol are considered to be model liquid fuels, biomass needs to undergo fundamental chemical changes before it is acceptable, since it contains significant portions of oxygen. Fast pyrolysis is a relatively technically mature process. Upgrading technologies are in the early stages of demonstration, and it is likely to be some time before they are deployed on a commercial scale.

The objective of this review is to present recent (2006 onwards) laboratory research and commercial developments in fast biomass pyrolysis and upgrading. It is beyond the scope of this review to cover theory behind processing operations and earlier research. For this, readers are referred to previous review publications e.g. fast pyrolysis [7–22], hydroprocessing [23–25], heterogeneous catalysts [1,26], applications of bio-oil [27,28].

2. Concepts for liquid transport fuel production via pyrolysis

Numerous discussions can be found in literature about the potential of substituting crude-oil feedstocks with biomass feedstocks [29–34]. One of the main problems associated with the use of biomass as a liquid fuel source is their delocalised distribution and poor energy density. This is exacerbated by the large scales of production on which biomass-to-liquid will need to be produced to produce an economically viable fuel [35]. One proposed solution is decentralised densification of biomass to bio-oil (and possibly stabilisation) followed by centralised upgrading. This model is being pursued by several pyrolysis companies. Centralised upgrading facilities might include existing crude oil refineries or dedicated 'biorefineries'.

Upgrading technology at centralised facilities might include gasification and synthesis, fluid catalytic cracking, hydroprocessing (hydrocracking and hydrotreatment), steam reforming, etc. (see Fig. 1). Envergent (www.envergenttech.com) is a joint venture pursuing a model of delocalised pyrolysis based on Ensyn's (Canada) Rapid Thermal Processing (RTP) Technology followed by centralised upgrading based on UOP Hydroprocessing Technology. They were allocated 25 m$ by the DoE for development of a 1 tpd demonstration unit at the Tesoro Corporation refinery in Kapolei, Hawaii with operations expected to begin in 2014 [36,37]. The plant will be an integrated fast pyrolysis and hydroconversion facility and aims to produce 4 barrels per day of gasoline, diesel and jet fuel. The commercial model is based on 4 RTP plants and one central upgrading facility [36]. Plans for 9 new plants based on Ensyn and UOP technology in Malaysia have also recently been announced [38]. Dynamotive (Canada, www.dynamotive.com), a well-known fast pyrolysis company, are also pursuing hydrotreating of bio-oil and a co-operation with IFP was recently announced [39,40]. The KIT (Germany) Bioliq concept is based on decentralised fast pyrolysis of biomass to bioslurry followed by gasification and synthesis of transport fuels at a central facility [41]. A demonstration plant is currently being developed. Tests have begun on the 12 tpd pyrolysis unit which was commissioned in 2008, and construction of

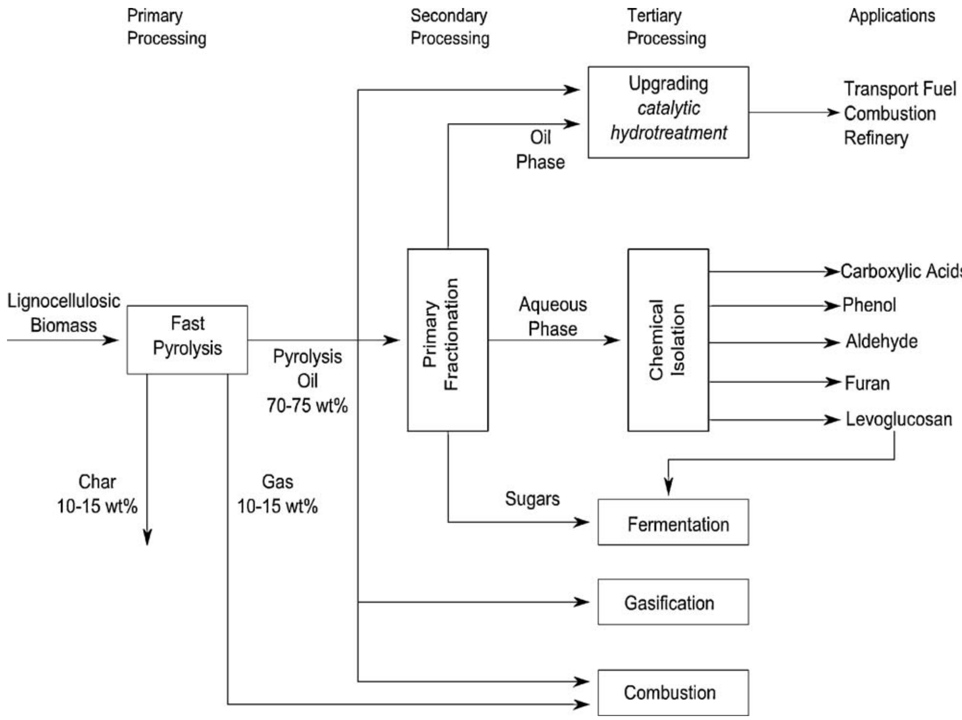


Fig. 1. The pyrolysis oil biorefinery [128].

the gasification and synthesis plants are expected to be completed by the end of 2011 [42]. PyTec (Germany, www.pytec.de) ablative technology would be particularly suited for decentralised densification and centralised upgrading since no carrier gases are required and it is likely to be feasible on a smaller scale. However the company appears to be pursuing power generation in modified engines rather than upgrading. The BTG (Netherlands, www.btgworld.com) biorefinery model is similar to that illustrated in Fig. 1.

Efforts are also being directed towards small-scale feasible solutions. The Metso/Fortum/UPM/VTT consortium is developing a concept which produces CHP and bio-oil [43,44]. Another solution might be the production of high quality fuel in a stand alone facility with upgrading technology. The IH^2 concept being developed by GTI (USA) proposes to reform a portion of the gases liberated from (1) the fast hydropyrolysis process and (2) hydropyrolysis vapour hydrodeoxygenation to provide the hydrogen required [45,46].

Another group of organisations are pursuing mobile fast pyrolysis solutions e.g. Agri-Therm (Canada), ABRI-Tech, and Renewable Oil International. More information on these organisations can be found in (Section 3.1).

Agrawal and Singh [47] and Singh et al. [48] propose that increased conversion efficiencies could be achieved by a natural gas reformer or coal-powered power plant to a fast hydropyrolysis facility, with the former facilities providing H_2/CO. This process was termed (the H_2Bio-oil process). Alternatively reliance on fossil-derived hydrogen required for fast-hydropyrolysis could be supplied by (1) solar splitting of water to H_2 (2) gasification of a portion of the biomass feedstock.

3. Biomass fast pyrolysis

3.1. Commercialisation of fast pyrolysis technology

The reactor is the core and most distinguishing piece of equipment for a pyrolysis process. Reactors are generally the most researched aspect of fast pyrolysis, though control and improvement of liquid quality and improvement of liquid collection systems are receiving increasing attention [12]. Currently only bubbling fluidised beds (BFBs) and circulating fluidised beds (CFBs) can be applied for commercial-scale production of biofuel [21]. While several reactors have been investigated on a laboratory scale and pilot scale no single reactor has emerged as being vastly superior to the others. That said certain reactors are more suitable for commercial application than others (see Fig. 2), and this has been reflected in commercialisation efforts.

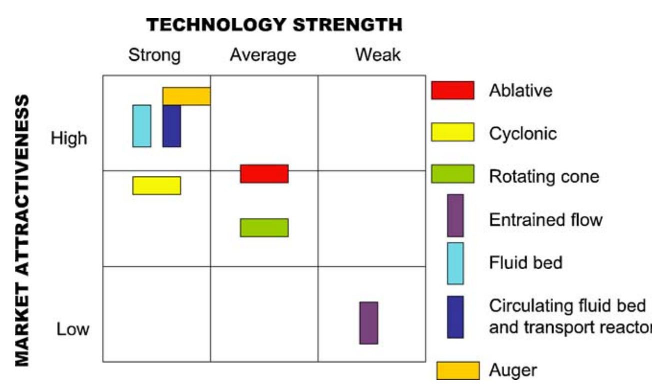


Fig. 2. Commercial potential of various fast pyrolysis technologies [182].

Fluid beds, circulating fluid bed and transport reactors, and auger pyrolysis reactors have a strong technology basis and high market attractiveness. The fast pyrolysis of biomass is at an early stage of commercialisation [49] with companies like Ensyn Technologies, Dynamotive, KIT and BTG leading developments [15,50]. Detailed information on various fast pyrolysis reactors can be found in previous reviews [8–15,21,22,51–53] and so will not be covered in this review.

3.1.1. Bubbling fluidised bed technology

bubbling fluidised beds (BFBs) exhibit consistent performance and product quality, with high liquid yields ranging between 70 and 75 wt% [8]. They are readily scaled up, though design modi-

fications need to be incorporated to account for temperature and concentration gradients observed with increasing height to diameter ratio of the reactor [14,21,54]. Numerous installations exist in various university and commercial facilities around the world [12]. At present dynamotive appear closest to commercial realisation of BFB technology. They have constructed 4 installations to date, the largest located at West Lorne (2006) and Guleph (2008), with design processing capacities of 100 tpd and 200 tpd respectively [12,55]. Operational performances of these plants cannot be found in literature, and it has been suggested that the West Lorne Plant has not reached its full design throughput possibly due to design and construction problems [15]. Biomass Engineering Ltd. (UK) are currently constructing 6 tpd modified version of a previous BFB design (by Wellman Engineering and Aston University, UK) which aims to overcome scaling problems associated with the Dynamotive design by surrounding the reactor walls with a char combustor [15]. Several BFB installations have been installed in China with throughputs ranging from 14 to 24 tpd [56–58]. Agri-Therm (Canada) offers a novel-design mobile pyrolyser to convert agricultural residue to bio-oil. The annular fluidised bed is heated by a cylindrical fluidised bed combustor. Lift tubes from the reactor to the combustor increase ablation and heat transfer to the solids. It is claimed the technology is ideal for pyrolysis of agricultural residues since discharge from the lift tubes drags low density particles down from the top of the bed [59]. Three 1–10 tpd units have been constructed, one of which is used for R&D [60].

3.1.2. Circulating fluidised bed conversion technology

While CFBs have similar features to BFBs a distinct difference is that the residence time of the char is almost the same for vapours ($\sim$1 s) [52]. The hydrodynamics are more complicated, but they are already used at very high throughputs in the petroleum and petrochemical industries [8,52]. Ensyn (Canada) are the leaders of CFB technology for biomass pyrolysis and have constructed a total of eight facilities to date based on their 'Rapid Thermal Process' [14]. While facilities based on this technology were operated on a commercial basis by Red Arrow Food Products Company (Wisconsin, USA) since 1989, current efforts are directed towards commercialisation of the technology for fuel production. The largest plant (100 tpd) was constructed in Renfrew, Canada in 2007 [55,61], they recently announced plans for construction of a 400 tpd plant [62]. Enverget is a joint venture (JV) between Ensyn and Honeywell/UOP founded in 2008 to improve Ensyn's capability to deploy RTP plants and to develop technology that allows the pyrolysis oil to be upgraded into a blend stock for processing in fossil-refinery infrastructure [61,63]. A Finnish Consortium involving Metso, Fortum, UPM and VTT are developing an integrated CHP/Bio-oil production concept, and tests are ongoing on a 7.2 tpd plant [50,64]. A fast pyrolysis reactor which appears to be a CFB is coupled with a fluidised-bed biomass boiler. The pyrolysis unit utilizes the hot sand in the fluidised bed boiler as a heat source, the bio-oil is quenched and the solids and fuel char are returned to the boiler where they are burned with fresh biomass [65]. The perceived advantages of such a bio-oil production model include (1) economic viability on a smaller scale than stand-alone plant; (2) a higher overall efficiency compared to standalone pyrolysis concepts; (3) lower investment costs and easier operation because a specialised char combustor is not required; (4) operation flexibility due to full exploitation of the by-product. It appears that the targeted application of the bio-oil is as a CHP fuel.

3.1.3. Rotary cone conversion technology

Rotary cone pyrolysis technology is applied by the Biomass Technology Group (Netherlands). The most recent overviews and updates can be found in literature [15,66,67]. Operational experiences were obtained on a 50 tpd Malaysian plant commissioned in 2006, but the plant is no longer running [15,68]. BTG are planning to demonstrate the technology in Europe on a scale of 120 tpd (about 125 MW_{th}), aiming to produce between 20,000 and 25,000 t/y of pyrolysis oil, electricity, process steam, and aqueous organic acids. This is taking place under the EMPYRO European Project [67]. Bio-oil Holding N.V. (Belgium/Netherlands) operates a100 kg/h plant and a 1500 kg/h industrial installation. Construction of two 5 tpd plants is underway, one in Holland and Belgium. The technology employed is similar to RCR technology by BTG, though the companies are no longer associated [15]. Feedstocks processed are mixtures of industrial wastes, SRF, mixtures of plastic/organic and inorganic mixtures [Personal Communication].

3.1.4. Auger conversion technology

The KIT Bioliq model comprises decentralised densification of biomass by pyrolysis (without solids separation), followed by centralised gasification and synthesis of methanol or DME [41,69]. A bioslurry of char and bio-oil is produced by a Lurgi–Ruhrgas twin screw mixer pyrolysis reactor. Being a relatively old technology considerable experience has been gained over the past 50 years (coal degassing or heavy crude coking). There is good potential for scale up [41]. A 12 tpd plant has been constructed in Germany in 2008 and while testing is underway [42], results have not yet been published. A recently presented economic analysis of the process calculated that biosyncrude production from dry lignocellulosic material have manufacturing costs of about €140/t; about 2/3rd of which are feedstock costs [69]. ARBI-Tech, a JV between Advanced BioRefinery Inc. and Forespect Inc. (Quebec, Canada) offer heating auger systems using a high density heat carrier. The units range in scale from 1 tpd to 50 tpd plants and it is expected that the first commercial 50 tpd plant will be operational soon [12,15,60]. Renewable Oil International LLC (USA) offers screw reactor technology and have built 4 units to date, the largest of which has a throughput of 4.8 tpd [12]. The economics of the process are presented in [70].

3.1.5. Ablative conversion technology

In the ablative pyrolysis process, wood is pressed against a rotating heated surface melting the wood and leaving behind an oil film which subsequently evaporates. No heat carrier is used and the process is limited by the rate of heat supply to the reactor rather than from the heat source to the biomass. Scaling is a linear function of heat transfer area so does not benefit from economies of scale of other systems [8,13,21]. PyTec (Germany) have built 2 ablative units, the largest of which is 6 tpd and fits in a 40 ft container. The company is targeting application of the bio-oils in a CHP unit running on a diesel engine [68]. An LCA for the PyTec BTO process was recently presented [68].

3.1.6. Comments on fast pyrolysis technology

A summary of fast pyrolysis developments are presented in Table 1. FP technology is close to commercialisation, there still appears to be scope for improvement. Scale-up of technology from laboratory is not always straightforward, and problems can be encountered. BFBs are being applied on large and small scale (i.e. mobile) applications. For large scale applications, it appears that some design and operational issues need to be resolved [15]. Alternative BFB designs continue to bedeveloped (e.g. the Agri-Therm annular FB with life tubes or the BFB with concentric char combustion by Biomass Engineering Ltd.). Feedstock quality is a critical parameter for fast pyrolysis operations. While wood has traditionally been considered the typical FP process feedstock, future processes may need to be feedstock flexible in light of constrained biomass availability.

The difficulties associated with processing high ash feedstocks at pilot scale are described by Venderbosch and Prins [15]. Realistic solutions for dealing with high ash feedstocks on an industrial scale

Table 1
Overview of fast pyrolysis developments.

Company	Technol.	Developments
Dynamotive	BFB	Several plants, largest is 200 tpd plant at West Lorne (CAN)
Ensyn	CFB	Several plants, largest is 100 tpd plant in Renfrew (CAN) [61]; Construction of 400 tpd plant in High Level, Alberta (CAN) with Tolko Industries LTD. announced [62]; Construction of 9 plants in Malaysia by 2015 announced [38]
BTG	RCR	120 tpd plant in Hengelo (NL) Announced [67]; Production of bio-oil, electricity, organic acids
B-O H N.V.	'RCR'	Largest plant is 12 tpd. Construction of two 5 tpd plants underway in NL and BEL [Personal Communication]
Biomass Eng.	BFB	4.8 tpd facility (UK) [15]
KIT/Lurgi	Auger	12 tpd pilot plant in Karlsruhe (GER) [42]
Pytec	Ablative	6 tpd plant (GER) [12]
ARBI-Tech	Auger	50 tpd plant to be commissioned soon [15]
ROI	M. Auger	4 units, largest 4.8 tpd [12]
Agri-Therm	M. BFB	3 units constructed 1–10 tpd [12]
Anhui Yineng	M/FB	Three 14 tpd units constructed (CHI) [12,56,57]
Metso Consort	CFB	7.2 tpd pilot plant at Tampere (FIN) [44]

need to be developed. Fast pyrolysis facilities require careful operation by skilled personnel who possess a good knowledge of the relationships between feedstock quality, process conditions, and the quality of the yielded bio-oil. Handling and storage issues and the current lack of large scale applications are the main barriers to development of a market for bio-oil [39]. New pyrolysis concepts like the IH^2 process by GTI or the bio-oil/CHP co-production model by Metso/Fortum/UPM/VTT have the potential to be disruptive technologies, if they can be successfully demonstrated and commercialised.

3.2. Review of recent fast pyrolysis laboratory research

Various reviews of laboratory research on fast pyrolysis of biomass are already available in literature [7,17–19,23,71]. This section aims to review some recent studies in this area.

3.2.1. Feedstocks for fast pyrolysis

At research level, hundreds of biomass feedstocks have been screened [7,8], though wood feedstocks are generally used for ease of comparison. Some feedstocks that have been experimented with on laboratory fluidised beds are summarised in Table 2. Properties of biomass feedstocks and the resulting bio-oil obtained from fluidised bed pyrolysis are presented in Table 3. While it is difficult to make generalisations, it can be seen that woody feedstocks generally produce the best quality oil in terms of C and H content and water content. The cultivar type of a particular biomass species [72], level of maturity [73], husbandry practices [74], seasonal variation [75] all influence the composition of the crop and consequently the physical and chemical quality of the bio-oil. Aquatic biomass is a novel feedstock for fast pyrolysis [75–78] though high ash, oxygen and nitrogen contents are a hindrance to obtaining a quality bio-oil product for fuel applications.

Table 2
Some feedstocks recently characterised on fluidised bed units.

Biomass type	Biomass
Woody	Iroko, albizia, beech, spruce [183], pine [92,110,114], white oak [113], larch [111], sawtooth oak [100], mallee [95,98,99], bamboo sawdust [184], pine, forest residues and eucalyptus [50], waste furniture sawdust [103]
Agricultural residues	Empty fruit bunches [66,80,81,185], soyabean harvesting residues [72], cotton-stalk [107], corn straw [186], corn cobs and stover [187], rice husk [102,105], rice straw [184], corncob, straw and oreganum stalks [188], maize stalks [106]
Industrial by-products	Grape skins and seeds [94], barley biomass/product streams [189], lignin [91]
Non-woody	Switchgrass [109], jute-stick [190], alfalfa, reed canary grass, eastern gamma grass [191], miscanthus [104], barley straw, rapeseed straw, reed canary grass [50]
Waste products	Guayule [192], soybean oil [193], fish waste [194], sewage sludge [195], chicken and turkey litter [196,197]
Marine	Seaweeds [78]

3.2.2. The influence of ash on pyrolysis

The ash content is one of the most influential parameters in the pyrolysis process. Agricultural residues and grassy-biomass generally have higher ash contents than woody-biomass. High ash contents in biomass pyrolysis feedstocks are not desirable because ash catalyses reactions which compete with biomass pyrolysis, leading to increased formation of water and gas at the expense of liquid organics [28,50,79–83]. It also reduces the temperature at which maximum organic liquids are yielded. Maximum levels of 3 wt% ash in feedstocks are recommended to avoid phase-separation of bio-oil during ageing [80]. The most problematic metal is potassium which has a strong catalytic effect [28,84]. Phosphorous also has an undesired impact on the yield structure and product quality [85].

One way to overcome the problem of high ash content feedstocks is by water or acid washing prior to pyrolysis [76,78–80,86–88]. This process decreases the ash content and results in a better quality bio-oil. For example for empty fruit bunches the yield of bio-oil can be increased from 50 wt% to 72 wt% by washing pretreatment [80]. Eom et al. [88] report increasing maximum degradation rates for washed biomass in the order HCl-treated biomass (1.55%/°C) > Deionised H_2O treated biomass (1.23%/°C) > Tap H_2O-treated biomass (1.19%/°C) > HF-treated biomass (1.15%/°C). Increasing levoglucosan and decreasing phenol, guaicol and syringol were observed in the treated biomasses. It is suggested that inorganics may catalyse cleavage of carbon-carbon linkage during pyrolysis of lignin. A recent study has shown that application of high levels of Nitrogen to a growing biomass crop is disadvantageous in terms of the quality of the resulting bio-oil produced because it results in a lower portion of cell wall components in the plant and higher levels of ash [74]. On commercial scales of application rain leaching of feedstocks in the field after harvesting could be considered [87].

3.2.3. The fate of lignocellulosic components in pyrolysis

The relative portions of cellulose, hemicellulose and lignin in biomass feedstocks have a significant influence on the quality of the bio-oil product. Agricultural residues generally contain less lignin and more hemicelluloses and ash/alkali metals than wood biomass, resulting in a higher O/C molar ratio than for woody biomass [50]. Cellulose contributes mainly to bio-oil production (72 wt% at 580 °C) by decomposing into sugars and water. Hemicellulose-derived bio-oil (mostly acids) yields are much lower (45 wt%) and produces significant quantities of char (25 wt%) and gas [89,90]. Since grasses and straw contain more hemicellulose than wood, gas formation is more significant with agricultural biomasses. Bio-oil from lignin has a lower oxygen content and therefore a higher energy density than conventional bio-oil [91]. So bio-oils from agricultural feedstocks have lower heating values than those form woody biomass (with a comparatively higher lignin content). On the other hand lignin is cracked better in agricultural feedstocks possibly due to the catalysing effect of alkali metals present in significant quantities.

Table 3
Summary of the properties of oil from laboratory fast pyrolysis reactors. Where multiple references for one feedstock are available, values are averaged. For feedstocks with more than one phase, values are also averaged. Abbreviations: Moist. = feedstock moisture, PT = pyrolysis temperature, P = number of phases in the liquid product, LY = liquid yield (organics and water), Acid. = acidity, E. Crops = energy crops, RCG = Reed Canary Grass, Tim. Grass = timothy grass, B. Straw = barley straw, FR = forestry residue, Oreg. Stalk = oreganum stalk, Bam. Sawd. = bamboo sawdust, EFB = empty fruit bunches, Jatrop. Shell = jatropha nut shell, Macroalg. = macroalgae (seaweed).

Feedstock						Oil									
	Moist. (wt%)	Ash (wt%)	C (wt%)	H (wt%)	O (wt%)	PT (°C)	P	LY (wt%)	C (wt%)	H (wt%)	O (wt%)	Water (wt%)	Solids (wt%)	Acid. (pH)	Reference
Hardwoods															
Albizia		1.8	46	6	46	475	1	55	42	7	50	25	3	2.9	[183]
Beech		0.7	47	6	46	475	1	63	41	7	51	22	0.2	2.5	[183]
Eucalyptus	7.6	0.4	50	6	44	500	1	82	42	8	50	21	0.09	2.2	[50]
Iroko		3.5	43	5	47	475	1	51	38	8	54	32	0.2	2.9	[183]
Larch	9	0.2	51	7	42	450	1	55	57	7	34	28	<0.005	2.1	[111]
Mallee		0.5	48	6	45	475	1	63	43	8	50	17			[95,98,99]
White Oak	10	2.0	50	6	43	410	1	50	55	6	19	31	<0.005	2.1	[113]
Softwoods															
Pine	11	0.2	47	6	46	488	1	69	49	8	44	23	0.01	2.6	[50,92,114]
Spruce		0.4	48	6	45	575	1	63	42	7	50	22	0.1	2.8	[183]
E. Crops															
RCG	10	3.1	46	6	49	500	2	68	39	8	53	25	0.2	3.3	[50,79]
Tim. Grass	3.9	3.2	47	6	46	500	2	53	32	9	59	39	0.01	3.4	[50]
Miscanthus	8	10	48	6	46	480	1	65	52	6	41	31.6	0.1		[74,104]
Switchgrass	8.3	4.3	45	6	50	500	1	64	38	7	54	25	0.8	2.87	[79]
Willow	7.8	1.3	48	6	46	507	1	70	43	7	50	17	0.4	2.68	[79]
Residues															
B. Straw	8.8	5.8	48	6	45	500	2	52	27	9	63	51	0.43	3.7	[50]
Corncob	2	1.6	43	6	48	488	2	43	47	9	49	23	3	3	[183,188]
Cotton Stalk	8	7				510	2	55	42	8	50	24		3.3	[107]
FR(Brown)	4.9	3.8	51	6	43	500	1	58	41	7	51	27	0.17	3.2	[50]
FR (Green)	8.1	2.1	51	6	42	500	1	64	41	8	50	26	0.09		[50]
Maize Stalk	8	8	49	6	43	500	2	66	44	6	48	23		3.2	[106]
Oreg. Stalk	9	4	43	6		500	2	32	45	6	38	6			[188]
Rice Husk	9	16	53	7	38	445	2	53	47	8	44	25	0.1	2.8	[102,105]
Rice Straw	7	9	43	6	49	430	2	68	33	6	61	35	<0.1	2.85	[184]
Wastes															
Bam. Sawd.	7	2	43	6	2	425	2		34	7	35	42	<0.1		[184]
Jatrop. Shell		3.0	50	7	38	480	3		42	9		34		3.33	[66]
EFBs	8	5	49	6	38	500	2	68	42	11	47.5	36			[80,81]
MacroAlg.															
Undaria	9.5	26	34	5	57	500	2	34	33.5	9	51	39			[78]
Lamira	8	29	30	5	62	500	2	38	47.5	9	39	45			[78]
Porphyra	6	10	40	5	47	500	2	47	41	7	43	30.5			[78]

3.2.4. Recent research in laboratory fluidised bed pyrolysis

References to recently commissioned fluidised beds can be found in literature: University of Maine (USA) [92], Pacific Northwest Laboratories (1 kg/h, USA) [93], University of Western Ontario (Canada) [94]; University of Monash (Australia) [95]; and the University of Twente [96]. Design features include spray condensing towers, packed scrubber towers, novel fractional condensation systems, novel feeding systems, process automation, etc.

Traditionally the goal of fast pyrolysis was assumed to be maximisation of the yield of liquid product. The liquid yield is influenced by parameters such as temperature, feed rate, and vapour residence time.

Many laboratory studies investigate a range of operational parameters and report the combination which maximises liquid yields. It can generally be stated that conditions maximising liquid yields are a pyrolysis temperature in the range of 400–550 °C and a vapour residence time of <2 s. Some recent studies investigating parameters have investigated the influence of variables in more detail. Increasing the solids retention time in the reactor can achieve satisfactory liquid yields at lower temperatures (56 wt% at 360 °C) [97]. As the pyrolysis temperature is increased, the content of water insoluble compounds, and consequently the molecular weight and viscosity of the bio-oil increase) [95,97,98]. This is thought to be due to increased conversion of lignin (since char yields decrease in this range). It is proposed the actual heating rates experienced by biomass (which decrease with increasing particle size) are an important factor in decreasing the yield of lignin-derived oligomers [99]. Lee et al. [100] found that optimum pyrolysis process conditions for collecting valuable chemicals like guaicols and syringols are a temperature of 400 °C, u_o/u_{mf} ratios of 3.0 and a bed length to diameter (L/D) ratio of 2.0. Other observations are that while increasing the feed rate of the reactor above its design capacity increases the bio-oil yield, the homogeneity of the oil decreases [101], and the use of pyrolysis gas as a fluidising medium increases bio-oil yields [102–104].

The configuration of the condensation system generally depends on the intended applications of the bio-oil product. The bio-oil can be condensed in one or several receptacles. Spray tower columns or packed bed scrubber towers can be applied for maximum condensation in the minimum amount of collectors e.g. [93,96,97,105–108]. On the other hand fractional condensation systems have the advantage of isolation of potentially valuable products for biorefinery applications [94,109]. Chen et al. [110] investigated selective condensation of bio-oil in four condensers and an electrostatic precipitator. Significant amounts of water were collected in the first condenser (86.5 wt%) of liquid product. Down the condenser train the water content decreased while the pH value, heating value and kinematic viscosity increased. Chemical characterisation of the liquid products illustrated selective condensation of specific compounds.

Hot gas vapour filtration can reduce the concentration of metals in bio-oils, though problems with clogging of the filter and catalytic decomposition of pyrolysis vapours by accumulated chars still need to be addressed. The removal of potassium from bio-oil remains difficult, possibly passing through the filter in vapour form [108]. A fluidised bed reactor with a cyclone and hot filtration system yielded bio-oil with low solids (<0.005 wt%) and metal contents [111–114]. Hot gas filters can be positioned inside [94,108] or outside the fluidised bed reactor [111–114].

4. Upgrading of pyrolysis vapours/bio-oils

4.1. Catalytic cracking of biomass/bio-oils

The use of heterogeneous catalysis in biofuel production processes increases selectivity to certain types of products. The main upgrading mechanism is the rejection of oxygen in biomass as coke or gas [26]. The resulting liquid product is generally more viscous than bio-oils derived by non-catalytic processes, and contains more aromatics. Readers are referred to previous reviews for more detailed information [26,29,34,115]. This section summarises some recent studies in this area.

4.1.1. Recent catalytic pyrolysis research

4.1.1.1. Micro-catalytic pyrolysis studies/catalyst screening. Carlson et al. [116] report catalytic pyrolysis of model biomass compounds with a ZSM-5 catalyst yielding 20–30% aromatics which are a valuable chemical feedstock. With pine wood catalytic fluidised bed pyrolysis with a ZSM-5 catalyst yielded 14% aromatics at a low space velocity and temperature of 600 °C. French and Czernik [117] conducted an extensive Py-GCMS study into zeolite upgrading of biomass. They compared 40 laboratory-synthesised and commercially available catalysts. Maximum hydrocarbon yields of 16 wt% (incl. 3.5 wt% toluene) were achieved with a nickel, cobalt, iron and gallium-substituted ZSM-5 catalyst. While ZSM-5 catalysts performed better than other zeolite catalysts, there was not a significant difference in performance between the synthesised catalysts and commercially available Zeolite 8014 catalyst. Torri et al. [209] used a novel Py-GC-MIP-AED system to evaluate and compare the performance of 31 different catalysts for catalytic pyrolysis. CuO, mixed metal oxide catalysts and ZnO reduced the proportion of heavy fraction in the bio-oil with minimum reduction in the bio-oil yield. Fisk et al. [118] recently evaluated the potential of supported platinum aqueous phase reforming catalysts for upgrading bio-oils. Pt/Al_2O_3 showed the highest deoxygenation activity, reducing the oxygen concentration of the model bio-oil from 41.4 wt% to 2.8 wt% after upgrading. The upgraded oil was highly aromatic, comprising of significant quantities of alkyl-substituted benzenes and cyclohexanes. The concentration of non-aromatic oxygenates was not significant.

4.1.1.2. Laboratory catalytic pyrolysis/upgrading experiments. Some recent vapour upgrading studies are summarised in Table 4. Generally speaking, upgraded bio-oil yields are lower (compared to non-catalytic processes) with increased formation of char/coke and gas. Upgrading of bio-oil post pyrolysis is also being investigated. The upgraded bio-oil is more viscous and has a higher aromatic character. A novel two stage bio-oil upgrading process was recently presented by Gayubo et al. [119]. The main objective of the concept design is to reduce deactivation of the upgrading catalyst thus extending its useful lifetime. The strategy is based on removing the pyrolytic lignin fraction of the bio-oil containing phenols which are well known to lead to coking of the catalyst. Catalyst deactivation is reduced and the pyrolytic lignin fraction with potential commercial value is isolated. The reactor can also be applied for olefin production [120]. By catalytic cracking of bio-oil with HZSM-5 in a batch reactor Hew et al. [121] obtained yields of organic liquid product and gasoline range product of 91.67 wt% and 46.67% respectively.

4.1.2. Commercial developments in catalytic cracking of biomass

The work group of George Huber at the University of Massachusetts have developed a process for the production of aromatics by catalytic pyrolysis of biomass. The technology is licensed by Anellotech, Inc. (www.anellotech.com) [122]. KiOR, a company based in Texas, offer direct biomass catalytic cracking technology. The target product is a bio-crude which can be processed in conventional refineries [26]. They are currently producing 15 barrels of biocrude per day at a pilot facility [123] and were granted funds for construction of five plants based on their technology in Mississippi, USA [124].

Table 4
A summary of some laboratory scale catalytic pyrolysis experiments.

Reactor	Catalyst	Comments	Ref
BFB (2 kg/h) with catalyst bed. Fresh catalyst charged to bed	HZSM-5 at 450–500 °C	Yield Structure: liquid (33 wt%), gas (53 wt%), char and coke (12.5 wt%); oils stable and have low viscosity; contain mainly phenolics, creosols, methyl substituted phenols; distillable (100% up to 640 °C) without char or solid formation; ageing not significant over 10 months. TAN number is 41 (compared to 90 for raw bio-oil)	[198,199]
BFB with catalyst bed	Beta, Y, ZSM-5, Mordenite	Catalyst structure influenced composition of oils but not the yield structure; ketones were higher and acids and alcohols lower over ZSM-5; mordenite yielded low amounts of polyaromatic hydrocarbons; most active deoxygenation: zeolite > Y > ferrite	[200]
BFB with separate upgrading zone within reactor	Zeolite	Bio-oil yield ranged between 43.5 and 52.7 wt%; more selectivity for organics directly related to more water and CO; most active deoxygenation: B-zeolite > Y > ferrierite	[201]
CFB pilot with catalyst regeneration	FCC catalyst	Bio-oil yield decreased (73–49 wt%) with introduction of catalyst; gas, coke and char production increased rapidly due to secondary reactions; catalytic bio-oils contain more hydrocarbons and less oxygenated compounds; FCC catalyst may be too active since it yielded a lot of water and coke	[143]
BFB and packed bed vapour upgrading	FCC catalyst	Lower amounts of acid (14.5–3.021 wt%) and increased aromatic hydrocarbons (0.488–16.795 wt%) compared to pyrolysis	[202]
BFB and fixed bed vapour upgrading	HZSM-5, HY, Ga/HZSM-5, Ga/HY	HZSM-5 more effective at upgrading the bio-oil than HY; oxygen mainly being converted to H_2O, CO, and CO_2	[203]
BFB with catalyst bed	CoMo-S/Al_2O_3	Max yield of BTXN was 6.3 wt% at 590°C	[204]
BFB with catalyst bed	HZSM-5	Max liquid yield was 56.8 wt%; oxygen content of oil was 14.69 wt%; H/C and O/C of oil was 1.51 and 0.15, HHV was 34.6 MJ/kg; reduced concentrations of ketones and phenols; dramatic increase in aromatics in oil (7.62–74.22 wt%)	[205]
BFB with catalyst bed	FCC	Optimal catalyst to biomass ratio was 1:10 for fresh FCC and 1:5 for spent FCC; max. oil yields for fresh FCC (11.8 wt%) catalyst and were lower than for spent FCC (18 wt%); hydrocarbons in the oil increased with increasing catalyst mass; less C and O were transferred to oil in presence of catalyst	[206]

4.1.3. Comments on catalytic upgrading

The problem of coke formation and catalyst deactivation are significant barriers to commercial deployment of catalytic cracking of biomass-derived products. fluid catalytic cracking (FCC) technology is frequently applied at large scales in oil refineries and possesses the ability to regenerate the cracking-catalyst. Positive results have emerged from exploration of the concept of hydrotreating bio-oil prior to fluid catalytic cracking. See Section 4.3 for more details. A summary of commercial developments in catalytic pyrolysis developments plus other upgrading strategies are summarised in Table 5.

4.2. Upgrading techniques involving hydrogen

4.2.1. Recent laboratory research in hydroprocessing

Readers are referred to previous reviews for background information [23–25,29,34]. It has already been established that optimal conditions for hydroprocessing of bio-oil are quite different to those for crude-derived products. A two-step hydroprocessing scheme comprising a mild stabilisation step and a more intensive upgrading step are envisaged. Alternatively, a hydroprocessing step coupled with a catalytic cracking is also being investigated. See Section 4.3 for more details. Current hydroprocessing research is focused on optimisation of the two-step upgrading process, reduction of hydrogen consumption, and the development of alternative catalysts rather than modification of traditional hydroprocessing catalysts.

4.2.1.1. American research in hydroprocessing. French and co-workers [125] targeted the production of an upgraded bio-oil with an oxygen content as high as possible while still meeting miscibility, volatility and acidity criteria for blending with crude oil in a refinery. Bio-oil was treated at 360 °C and 17 MPa in a two step (stabilisation and hydroprocessing) batch process yielding 36% light product with 7% oxygen and 30% liquid residue. Hydrogen consumption was about 3% and the light fraction yielded had acceptable TAN and hydrocarbon miscibility. 36% of the carbon from the feed oil was captured in the light liquid product with additional 30% in the residual liquid product. Elliot and Hart [126,127] tested various catalyst formulations over a range of operating parameters (temperature, pressure and flow rate with bio-oil from several different feedstocks. Separate hydrotreating and hydrocracking experiments were conducted in separate reactors and then both steps were incorporated into a non-isothermal reactor system. The hydrotreating step employed a Pd/C catalyst, while the hydrocracking employed standard hydrocracking catalysts and refinery conditions based on UOP technology. While the hydrotreated bio-oils closely resembled the bio-oil feedstock and parent biomass, there was not much of a difference between the oils after hydrocracking which contained similar collections of primary cyclic hydrocarbons. Further conclusions from work at PNNL are that the residual oxygen content correlates directly with the processing space velocity and the gasoline range product yield directly correlates with the processing space velocity [36].

4.2.1.2. European research in hydroprocessing. Insights into catalytic hydrotreatment at University of Twente/BTG/University of Gronigen were recently presented [128–130]. Initial work for the Biocoup Project in hydroprocessing focused on the application of a Ru/C catalyst for hydrodeoxygenation (2002–2009) [129]. Results achieved were more favourable than those achieved with traditional petroleum hydrotreating catalysts. It was found that competing reactions occur during hydroprocessing. The first is a thermal pathway which yields high molecular weight components and coke which deactivates the catalyst. The second set of reactions are hydrotreating and hydrocracking reactions which improve the quality of the product. Recent efforts have focused on the development of catalysts which suppresses the thermal reactions and promote hydrodeoxygenation. This approach has shown positive results including (1) a lower MCRT over the complete oxygen-content range (2) similar molecular weight as original bio-oil over complete oxygen-content range (3) lower viscosity over complete oxygen range and (4) higher hydrogen transfer at similar operating conditions. Venderbosch et al. [131] report hydroprocessing and high pressure thermal treatment (HPTT) on a novel high pressure reactor. It was suggested that parallel reactions like re-polymerisation, decarboxylation and hydrotreating occur up

Table 5
Developments in bio-oil upgrading. Abbreviations: CP = catalytic pyrolysis, FP = fast pyrolysis, HP = hydroprocessing, FCC = fluid catalytic cracking, IH^2 = catalytic hydropyrolysis and vapour hydrodeoxygenation, VU = vapour upgrading, G = gasification, S = synthesis, IP = intermediate pyrolysis, U = upgrading, SR = steam reforming.

Company	Process	Developments
Anellotech	CP	Reported to be developing a 2 tpd plant (planned construction completion in 2014) [207]
Envergent	FP + HP	Demonstration 1 tpd hydrotreating plant in Kapolei, Hawaii, expected commissioning in 2014 [36,138]
KiOR	CP (FCC)	1 tpd pilot plant in Texas. Funding for 5 Plants in Mississippi [124]
GTI	IH^2	Proof of principle on laboratory scale. DoE Funding recipient [45,46,138]
RTI	VU	Lab-scale entrained flow pyrolysis reactor for catalytic vapour upgrading. [138,208]
KIT	FP + G + S	12 tpd FP plant constructed. G + S unit expected to be constructed by 2012 [42]
Choren	IP + G + S	45 MW_{th} demonstration facility – intermediate pyrolysis + gasificaiton + synthesis;
BTG/ Groningen/Twente	FP + U	Bio-oil gasification trial completed on Choren gasifier (GER) [15]. Development of hydroprocessing catalysts [129]
REII	CP + SR	Developing 25 tpd pilot plant (Toledo, Ohio) for advanced pyrolysis and steam reforming for diesel and gasoline [138]

to 250 °C. Repolymerisation reactions which liberate water occur on a faster timescale (minutes) compared to hydrotreating reactions (10 s of minutes, hours), whereas repolymerisation to char components is the result in an absence of hydrogen and catalyst, production of stabilised components that can be further upgraded result when hydrogen and catalyst are used. It was proposed that decarboxylation via FCC may be more desirable for further upgrading due to the high costs associated with hydroprocessing. De Wild et al. [132] performed fluidised bed pyrolysis of lignin followed by hydrotreatment with a Ru/C catalyst. This is particularly interesting from a biorefinery perspective. At pyrolysis temperatures of 400 °C up to 21 wt% of a phenolic fraction containing 10 wt% of several phenols was yielded. Cycloalkanes, cyclohexanes and alkanes were produced in the hydrotreating step.

Mahfud et al. [133] developed a liquid phase ruthenium catalysts for the hydrotreatment of the aqueous phase of bio-oil at mild conditions (50–90 °C and 2–4 MPa). Model bio-oil compounds were used and upon reaction amounts of reactive aldehydes were reduced significantly. Wildschut [134] compared traditional hydrotreating catalysts and relatively novel noble metal catalysts under mild and severe hydrotreating conditions. Highest oil yield with an Ru/C catalyst (65 wt%) was obtained after 4 h using a 5 wt% catalyst to pyrolysis oil ratio, temperature of 350 °C and 20 MPa. It was concluded that catalytic hydrotreatment is a relatively slow process and takes place on a timescale of hours. Repeated use of the Ru/C catalyst in hydrotreating experiments resulted in decreased liquid yield, increased solids, a reduction in H/C and less methane in the gas phase. Hydrodeoxygenation of model bio-oil compounds were investigated by Wildschut et al. [135] under conditions of 250 °C, 10 MPa for 4.3 h with an Ru/C catalyst. Two parallel reaction pathways were observed, a thermal non-catalysed pathway and a hydrogenation pathway leading to smaller polyols and gaseous hydrocarbons such as methane and ethane. The catalytic hydrotreatment route is preferred over the thermal route leading to solids. Addition of acetic acid increased the solids content. Wildschut et al. [136] screened a number of noble metal catalysts for hydrotreating bio-oils including. The mild hydrotreating step was carried out at 250 and 350 °C at hydrogen pressures of 10 and 20 MPa. The Ru/C catalyst was found to be superior to classical hydrotreating catalysts in terms of oil yield (60 wt%) and deoxygenation (90 wt%). Upgraded oils had lower organic acids, aldehydes, ketones, and ethers than the feed, but phenolics, aromatics and alkanes were higher. Highest oil yields (65 wt%) were obtained after 4 h using 5% wt intake of catalyst on fast pyrolysis oil. The carbohydrate fraction of the oil appears to be very reactive [130]. The H/C ratio of the oil appears to be a function of the reaction time and increases with time. The amount of hydrocarbon fraction is time dependent and is maximised after 4 h operation.

Yakovlev and co-workers [137] developed and tested a series of catalysts for hydroprocessing oxygenated liquids. A new bifunctional non-sulfided Ni–Cu catalyst was developed. Some of the developed catalysts were subjected to hydrodeoxygenation tests on bio-oil from VTT were performed at the University of Groningen and substantial oxygen decreases were observed, from 40 to 5 wt%. Oasmaa et al. [43] investigated new analytical techniques for hydrodeoxygenated bio-oils. They report that during stabilisation no change in the composition of the acids was observed. On the other hand, aldehydes and sugars were hydrogenated to alcohols (seen as an increase in the diols, which then decreased with increasing severity of treatment). Heeres [128] recently discussed the influence of the pyrolytic lignin fraction of bio-oil on hydrotreating reactions and products. Catalytic hydrotreatment results in a strong reduction in the carbohydrate and a big increase in extractives. The extractives are composed of alkanes > phenolics > alkylbenzenes. The alkane fraction is composed of linear alkanes (hexane, heptane, none and higher alkanes), cyclopentates, and cyclohexanes. The pyrolytic lignin fraction of the bio-oil does not appear to be responsible for high molecular weight compounds and char. During HDO of pyrolytic lignin, no solids, more water and no gas composition effects were observed. Pyrolytic lignins are responsible for significant quantities of phenolics and alkanes. Instead the carbohydrate fraction is likely to be responsible for the char formation in hydroprocessing [128]. A summary of developments in hydroprocessing is presented in Table 6.

Table 6
Some findings from recent hydroprocessing studies.

- Bio-oils from different feedstocks and reactors are similar after HP [36,126]
- Oxygen and gasoline range products in upgraded oil directly proportional to space velocity [36,126]
- Noble metal catalysts on carbon achieve better deoxygenation than traditional catalysts [130,131,136]
- Repeated catalyst use decreases liquid yield and H/C ratio with increased solids [134]
- Upgraded oils contain lower quantities of organic acids, ketones and ethers. Phenolics, aromatics and alkanes are higher [130]
- Newly developed catalysts reduce oxygen content with limited increases in MCRT and viscosities [129,137]
- Lignin portion of the bio-oil is not responsible for residue. It forms phenolics and alkanes. The carbohydrate fraction of bio-oil is very reactive [128,132]

4.2.2. Fast hydropyrolysis

Concepts for hydropyrolysis have already been discussed. The IH^2 process is currently being developed by GTI [45,46]. The process comprises three stages: (1) biomass hydropyrolysis under medium hydrogen pressure in the presence of a novel glass ceramic catalyst; (2) hydrodeoxygenation of hydropyrolysis vapour with a conventional sulfided HDS catalyst under mild conditions; (3) reforming of C_1–C_3 hydrocarbon gases liberated from the previous two steps yielding the necessary hydrogen for the reactions. The hydrocarbon liquid yield is 24–28 wt% which is comparable with fast pyrolysis coupled with FCC or HDO. It is highly deoxygenated and contains no polynuclear aromatics, olefins, or reactive free radicals because high partial pressures of hydrogen and catalyst are available dur-

ing conversion. GTI were recently allocated 3 m$ to investigate this further [138].

4.3. Integrated upgrading approaches and co-processing

4.3.1. UOP/PNNL/NREL

Integrated processing strategies are likely to be required for producing liquid transport fuels from bio-oils. These include hydrotreating followed either by co-processing in a HDS or FCC unit with heavy crude-derivatives. UOP with PNNL and NREL have investigated various possibilities for upgrading bio-oil [139–141]. For hydrotreating a UOP Ni–Mo and PNNL Pd/C catalyst were examined. The UOP catalyst was more active for oxygen removal at lower pressures. Hydrocracking was undertaken with a Ni–Mo catalyst. The hydrotreating/hydrocracking combination reduced oxygen content to 4%. Co-processing of bio-oil, the pyrolytic lignin fraction of bio-oil and a hydrotreated bio-oil with VGO were simulated on an ACE reactor. Bio-oil, pyrolytic lignin and hydrotreated-pyrolytic lignin all produce more coke than VGO. With blends of VGO and bio-oil or pyrolytic lignin, the acidity appeared to increase crackability of co-processing feed towards the light end of the spectrum. The neat hydrotreated pyrolytic lignin had high levels of coke. Coke production levels were acceptable at 5% blends of hydrotreated bio-oil with VGO [139].

4.3.2. Amherst-MA, USA

The working group of Huber at Amherst-Massachusetts are investigating the coupling of fast pyrolysis, hydrotreating, and catalytic cracking for the production of commodity chemicals. In a significant development, the group found that coupling hydrotreating of bio-oil with catalytic cracking yields of aromatic hydrocarbons and light olefins in quantities up to three times greater than catalytic cracking of raw bio-oil [142].

4.3.3. CPERI, Greece

Lappas et al. [143] summarise research into co-processing CPERI (Greece) which goes back to a previous collaboration with Veba Oel [144]. A combined HDO step and co-processing in an FCC unit produced on-spec transport grade fuel. Bio-oil was subjected to a thermal hydrogen processing step, and co-processed with VGO in a pilot FCC unit. The nozzle plugged under continuous operation, so the heavy fraction of fast pyrolysis liquid (HBFPL) was diluted with light cycle oil (LCO) (15/75) and blended with vacuum gas oil (VGO) (at 15/75). FCC of VGO was the reference case for comparison. Coke production was higher, and liquid petroleum gas (LPG) yields were lower, and an increased selectivity towards gasoline and diesel were observed when bio-oil is in the feed. The gasoline contains more aromatics and less paraffins and olefins compared to gasoline with no bio-oil. Reduced conversion was observed due to heavier components in the oil.

4.3.4. The Biocoup project, Europe

Considerable research in the area of co-processing has been undertaken as part of the Biocoup project (http://www.biocoup.com/) 2006–2011 and developments are discussed in the following paragraphs.

Bui et al. [145] studied the co-processing of bio-oil and petroleum model compounds under HDS conditions. They observed decreasing catalyst performance at low temperature and high contact time, though to be due to intermediate phenols competing with sulfur containing molecules on dehydrogenation sites. It was concluded that co-processing of crude-derivatives and HDO oil in a HDS unit is possible. The molecular weight distribution is similar but competing reactions between HDS and HDO may reduce the efficiency of the process [145,146]. Fogassy et al. [147] investigated the possibility of adding 20 wt% HDO oil to VGO feedstock for fluid catalytic cracking. Comparable gasoline yields were observed to an unblended VGO feedstock. However, since hydrogen is consumed in deoxygenation reactions from the VGO feedstock, the final product is poorer in hydrogen and contains more coke, aromatics and olefins.

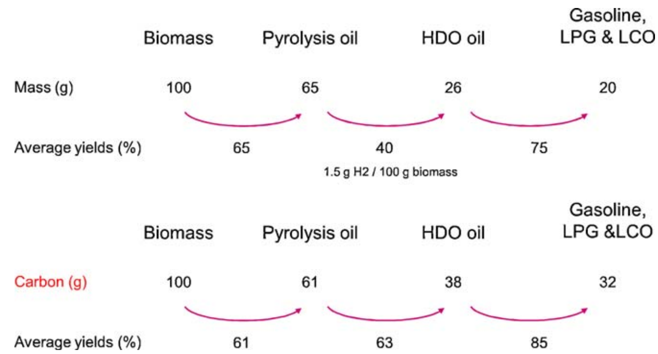


Fig. 3. Average mass and carbon efficiencies associated with combined HDO and FCC approaches [150].

de Miguel Mercader et al. [148] report results from an investigation in the high pressure thermal treatment (HPTT) of bio-oil in a continuously fed reactor. Because direct co-processing of bio-oil results in an FCC unit results in excessive char formation and unacceptably low yields of gasoline, an intermediate upgrading step is required. HPTT was investigated as a means of producing oil that can be co-fed to a standard refinery. Despite significant reduction of oxygen and water content the HPTT oil was immiscible with a conventional heavy refinery stream (Long Residue), so further co-processing by HDO would be required before co-processing in a refinery. Process temperature had a significant influence on the yield and properties of the oil. The need for HDO of HPTT oil was confirmed by de Miguel Mercader and co-workers [149] who observed high coking rates with HPTT in a MAT reactor. In the same study they found that HDO of bio-oil followed by co-processing with petroleum residues in a FCC shows good potential. The MCRT (tendency to coke) of a mildly hydrodeoxygenated bio-oil mixed with Long Residue improves to a greater extent than what might be expected by a simple additive effect. It is suggested that MCRT and the H/C ratio of hydrodeoxygenated bio-oils should be the parameters defining quality of such oils for subsequent FCC. While HDO has traditionally aimed for maximum deoxygenation, the authors experienced problem-free co-processing of the upgraded oils with long residue (20/80 blend) despite the fact that the oxygen content of the upgraded oils were 28 wt%. The advantage with this process would be less hydrogen consumption (here it was 278 l H_2/l of bio-oil) compared to a double hydrotreating–hydrocracking process.

A recent summary of co-processing in the Biocoup project was presented by Hogendoorn et al. [150]. The main conclusion is that the HDO oil from whole oil, and the organic phase and aqueous phase differ considerably in terms of MCRT, molecular weight and H/C ratio, but not so much the oxygen content. Another is that increasing HDO severity increases carbon/energy recovery and reduces the oxygen and water content. For co-processing of HDO oils in a HDS system, the molecular weight distribution after HDS is similar using different HDO oils, and there is competition with desulphurisation. The carbon and energy transfer efficiencies of fast pyrolysis, hydrotreating and catalytic cracking are illustrated in Fig. 3.

4.3.5. Comments on integrated co-processing

Integrated co-processing would provide a relatively straightforward route to the production of liquid transport fuels via

fast pyrolysis since oil refining infrastructure is already available. Some modifications would however be necessary. Additionally synergistic effects between co-processed feedstocks may increase efficiencies and reduce the intensity of processing required. Combined hydrotreating and catalytic cracking appears to possess significant potential for the production of commodity chemicals. However this is a relatively new area of research and requires more investigation.

4.4. Developments in upgrading bio-oil by steam reforming

Steam reforming technology can be applied to bio-oils for the production of syngas [151–154]. Reactions generally take place at a high temperature (600–800 °C) and high space velocities are usually employed with a Ni catalyst. Deactivation of the catalysts by coking is seen as one of the main problems of the technology. Renewable Energy Institute International (REII) are working on demonstration of advanced pyrolysis and steam reforming producing diesel and gasoline from biomass. Their demonstration plant will process 25 tpd and be located at Toledo Ohio [138].

4.5. Developments in upgrading bio-oil by gasification and synthesis

Some companies and research organisations are pursuing a decentralised densification/centralised gasification and synthesis model. Recent research has shown that pressurised fluidised-bed gasification of bio-oil followed by catalytic reforming can readily be used to convert bio-oil to syngas [155,156]. Westerhof et al. [97] recently investigated how the pyrolysis temperature influences the physical properties of the resulting bio-oil, and the consequent ease of atomisation for a gasification system. They found that the oil obtained at 360 °C produced less char, 2 versus 5 wt% compared to the oil obtained at a pyrolysis temperature of 530 °C, so the oil produced at 360 °C has a better quality under the atomisation conditions (850 °C and droplet sizes of ±50 μm). Czernik et al. [151] achieved a 70–80% of the stoichiometric potential of hydrogen from catalytic gasification of bio-oil in a fluidised bed reactor. KIT, developers of the bioliq process, plan to finish construction of a demonstration bioslurry gasification, gas cleaning and synthesis plant in 2012 [42]. R&D into gasification of bio-oil on a 500 kW_{th} entrained flow gasifier owned by Chroen has been undertaken by BTG, but results are not yet reported in literature [15].

4.6. Mild stabilisation techniques for bio-oil

4.6.1. Developments in bio-oil filtration

It is well known that char and ash particles in bio-oil contribute to instability. Javaid et al. [157] and Ford et al. [158] applied liquid-phase microfiltration processes to remove char particles from bio-oil to sub-micron levels. Results demonstrate the removal of the major quantity of char particles with a significant reduction in overall ash-content of the bio-oil.

4.6.1.1. Developments in bio-oil esterification. The highly acidity and chemical instability of bio-oils impose severe limitations on the extent to which they might be processed in a refinery. One way to address this is by treating the bio-oil it with a low-cost alcohol (e.g. methanol, ethanol or butanol) in the presence of an acid catalyst (optional), converting the carboxyl and carbonyl groups to esters and acetals (or ketals) respectively [159–161]. Recent approaches described hereafter have attempted to catalyse and increase the severity of the reaction conditions to improve conversion. The reactions are equilibrium driven, so the reaction products are unstable. This might be overcome by removing the either the water or reactants by either (a) removing the water by use of molecular sieves or azeotropic distillation or (b) by reactive distillation removing the esters and acetals and the water is left in the bio-oil [162]. A recent approach to uncatalysed esterification/solvent addition is an *in situ* process involving contact of biomass pyrolysis vapours from an auger reactor with an atomised ethanol spray [163].

4.6.1.2. Developments in acid-catalysed esterification. A number of recent studies have examined acid catalysed esterification of bio-oils in alcohols [162,164–167]. The main advantage here compared to simple solvent addition is much higher conversion of undesirable compounds, thus resulting in bio-oils with significantly improved properties. Conversion can be increased even further by esterification in supercritical ethanol [165,166]. Other approaches to improve the conversion centre on product removal. Since esterification and acetylisation reactions are equilibrium reactions, increasing concentrations of esters, acetals and water will tend to shift equilibrium back towards the original reactants. A solution to this problem is to remove the reaction products as they are formed by azetropic water removal or reactive distillation [162,164].

Catalysed esterification applies less severe reaction conditions than hydroprocessing and fluidised catalytic cracking, and this is reflected in the moderately upgraded bio-oil product. Tang et al. [166] used a combination of upgrading processes for hydrogenated catalysed ($Pd/SO_4{}^{2-}/ZrO_2/SBA15$) esterification of bio-oil in supercritical ethanol. Other problems with esterification are the instability of the produced acetals in bio-oil and their tendency to revert back to carbonyls [162]. Lohitharn et al. [167] found that aldehydes inhibit the esterification of acids at lower temperatures. Junming et al. [164] obtained a good quality product from esterification of bio-oils catalysed by $SO_4{}^{2-}/M_xO_y$ and H_2O_2 in a reactive distillation column. The minimum TAN that Moens et al. [162] could achieve from various approaches to catalysed esterification and removal of products was 20. This exceeds, by a factor of 10 the TAN allowed for oil refinery feedstocks. They suggested that this approach has limited potential. Other recent advances include the development of a new mesoporous catalyst functionalised with propysulfonic acids for esterification, effective for acetic acid conversion [168]. Wang et al. [169,170] investigated esterification of bio-oil with 732- and NKC-9-type ion-exchange resins. They proposed Acid Number Determination as a means of assessing the potential of oils to be upgraded and the effectiveness of the upgrading process. Discrepancies were observed in pH measurements of the upgraded oils – in fact the pH was found to have decreased after esterification. Acid numbers of the bio-oil were decreased by 88.54 and 85.95% respectively, representing the conversion of organic acids to esters.

5. Application of oils/upgraded oils as transport fuels

Applications of bio-oils are already reviewed [27,28]. This section aims to summarise recent studies in this area.

5.1. Developments in blending bio-oil with other fuels

Nguyen and Honnery [171] found that fast pyrolysis bio-oil can be mixed up to 20 wt% with ethanol and combusted at elevated pressures (2.5 MPa at 827 °C) without any significant drop in performance. The argument for this approach was that combusting bio-oil with ethanol in ethanol modified engines would reduce problems associated with combustion of 100% bio-oil. Peak pressure was slightly higher and burning rates were similar to 100% ethanol blends. 40% bio-oil caused instability and increased particulate loads were observed. Honnery et al. [172] investigated the properties and combustion of a fuel made by direct blending of the heavy tar fraction from slow pyrolysis of biomass with diesel. Tests were conducted on a 4-cylinder 4-stroke DI diesel engine at

speeds of (2000 rpm). They readily obtained stable blends of 20 and 40% pyroligneous tar in diesel without the use of surfactants. There was little difference in performance with the 20% blend, but for the 40% blend a higher in cylinder gas temperature and pressure was observed. Ignition delays were also noted. The potential for bio-oil and bio-diesel blends has also been investigated [173,174]. An aqueous phase and heavy oil fraction were produced. Water was removed from the light phase and 5 wt% methanol was added to both fractions. Bio-oil: bio-diesel blends were made with 10, 20, 40 and 50% bio-oil (light and heavy fractions separately). The fuel properties did not change greatly though small increases in density and viscosity were observed. The acidity was reduced by addition of HCO_3.

Developments in emulsification of bio-oils have already been summarised [28,175,176]. Recent studies by Jiang and Ellis [177,178] report emulsification of bio-oil with bio-diesel. Optimal conditions for obtaining a stable mixture were realised with addition of 4% octanol surfactant by volume to a 4:6 bio-oil/bio-diesel ratio by volume, stirring at 1200 rpm for 15 min at 30 °C. After emulsification treatment the water and high molecular-weight components remained in the bottom (pyrolytic-lignin-rich phase) thus being removed from the upper bio-oil/biodiesel mixture. There are other references to emulsification of bio-oil in recent literature [105–107]. An interesting development is the stabilisation of emulsions and catalysis of reactions at the liquid/liquid interface with recoverable nanoscale catalysts [179,180].

5.2. Developments in combustion of bio-oils and upgraded bio-oils

The direct use of bio-oil in diesel engines is possible, but with significant modifications [181]. PyTec (Germany) are developing combustion of raw bio-oils in modified diesel engines [68]. There is very little information available about combustion of upgraded bio-oils in literature. This may be due to the fact that that most upgrading is being undertaken on a small scale and sufficient quantities may not be available for testing. However, larger quantities of upgraded bio-oils should become available in the future, and tests are planned [15,136].

6. Conclusions

Fast pyrolysis of biomass is verging on commercial application. Demonstration of upgrading technologies is underway, though it may be some time before they are deployed on an industrial scale. In terms of fast pyrolysis reactors, no one reactor appears to be vastly superior to the others, though certain reactors may be more suitable for particular applications and scales of application than others. A wide range of feedstocks have been tested for fast pyrolysis with wood giving the best quality oil. High ash content is a significant technical barrier for the production of a quality product from poorer quality biomass e.g. agricultural residues. Acid washing, water leaching, hot gas filtration, and post pyrolysis filtration can improve the quality of the resulting bio-oil, but more research in this area is required. It is also apparent that the chemical composition of biomass feedstocks for fast pyrolysis can vary significantly between and within different species. Maximisation of the liquid yield from fast pyrolysis, the traditional goal, may need to be reconsidered when the desired properties of the bio-oil as well as downstream processing requirements are taken into account.

The integrated bio-oil/CHP concept by the Metso/ Fortum/UPM/VTT consortium and the IH^2 concept by GTI are particularly interesting prospects for increasing the feasibility of smaller scale operations. On the other hand, the decentralised densification/centralised upgrading concept appears to have a realistic potential offsetting transport fuel consumption, provided the upgrading technologies can be successfully demonstrated. There appears to be an increasing interest in synergies between technologies in integrated biorefinery products e.g. biomass or bio-oil fractionation followed by biochemical and thermochemical conversion routes. The energy and carbon transfer efficiencies of fast pyrolysis coupled with upgrading technologies seems low (30–40%). Coking of the catalyst in biomass or bio-oil catalytic cracking remains an issue, and research in this area is continuing. Fractionation of bio-oil prior to catalytic cracking may help overcome this issue.

A number of interesting insights into bio-oil hydroprocessing have been gained in recent years. An important one is that upgrading should selectively target problematic oxygen functionalities rather than reducing the total oxygen content of the oil. While work in this area is continuing, future research will need to address the search for cheap (i.e. non precious metal) catalysts. Integrated upgrading approaches i.e. hydroprocessing followed by fluid catalytic cracking appears to possess synergistic benefits. The production of commodity chemicals via hydroprocessing and catalytic cracking routes within the biorefinery infrastructure may enhance the economic viability of pyrolysis and pyrolysis-related processes. While milder intensity upgrading approaches may be applied in niche applications, it is unlikely that the quality of the resulting bio-oil will be acceptable for refiners or end-consumers alike.

Acknowledgement

This study was funded under the Charles Parsons Energy Research Program (Grant Number 6C/CP/E001) of Science Foundation Ireland (SFI).

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